BIOMASS AND RENEWABLE FUELS

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ABSTRACT

Biomass is an important contributor to the world economy. Agriculture and forest products industries provide food, feed, fiber, and a wide range of necessary products like shelter, packaging, clothing, and communications. However, biomass is also a source of a large variety of chemicals and materials, and of electricity and fuels. About 60% of the needed process energy in pulp, paper, and forest products is provided by biomass combustion. These processes could be improved to the point of energy self-sufficiency of these industries. Today's corn refinery industry produces a wide range of products including starch-based ethanol fuels for transportation. The biomass industry can produce additional ethanol by fermenting some by-product sugar streams. Lignocellulosic biomass is a potential source for ethanol that is not directly linked to food production. Also, through gasification biomass can lead to methanol, mixed alcohols, and Fischer-Tropsch liquids. The life science revolution we are witnessing has the potential to radically change the green plants and products we obtain from them. Green plants developed to produce desired products and energy could be possible in the future. Biological systems can already be tailored to produce fuels such as hydrogen. Policy drivers for increased use of biomass for energy and biobased products are reviewed for their potential contributions for a carbon constrained world.

INTRODUCTION

In the future, our energy systems will need to be renewable and sustainable, efficient and cost-effective, convenient and safe. Can the integrated development and use of our nation's biologically-derived renewable resources contribute significantly to our energy independence, increased energy diversity, and reduced carbon emissions while at the same time fostering rural development, technological innovation and commercialization?

We address biomass, derived fuels and energy, and biological hydrogen production.

TODAY'S BIOMASS ECONOMY FROM AN ENERGY VIEWPOINT

The United States consumes about 94.2 quads (1 quad = 1 quadrillion Btu = 1.055 EJ) of all forms of energy self generated or imported. Of those, 7.1 quads are renewable energy. More than 3 quads provide residential and commercial heat, heat and power in industry, direct electricity production, as part of the energy and environmental services in residue disposal and landfill gas use, and transportation fuels from biomass. These various sources of bioenergy and their relationship with the conventional biomass industries are shown in Figure 1 [1].

As a primary energy source, biomass (43%) is just behind hydropower (51%) among the renewable resources. The Public Utilities Regulatory Policy Act (PURPA) of 1978 provided the incentive for industry to invest $15 billion, establish 66,000 jobs and create a biomass power industry worth $1.8 billion/year (see Figure 2). A total of 0.75 quads or 1% of U.S. electricity is from biomass power, and more than twice that amount of energy is generated and used within the forest products industry. Waste to energy represents another 0.5 quads. More than a thousand biomass facilities generate electricity or cogenerate for their own use [2].

Utility restructuring is challenging many of these operations because of competition with facilities in which capital costs have already been amortized and can produce electricity at lower costs. Some and added bioenergy capacity cannot compete on cost alone because natural gas-fired combined cycle plants have lower capital cost and moderate fuel costs
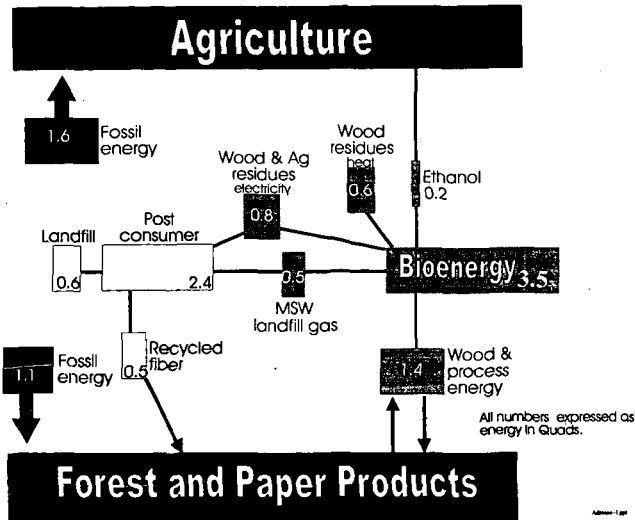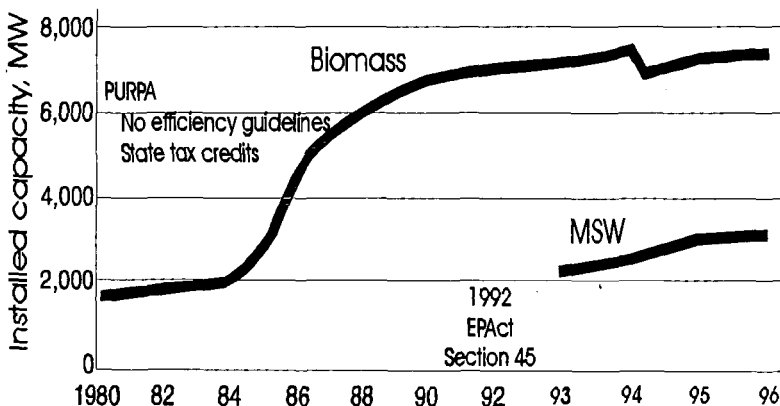
Figure 1. United States Bioenergy (1997)

Figure 2. Electricity from Biomass in the United States.

and are predicted to be stable. One way in which bioenergy can be helped is by finding ways to pay for the environmental service it can provide such as landfill avoidance. Another way is the renewable portfolio standard, which ensures a minimum level of renewables in the electricity portfolios of power suppliers in implementing jurisdictions.

Today's bioenergy industry also produces liquid fuels, primarily ethanol, using approximately 6% of the corn grain produced each year. Production started in the late 1970s and capacity has increased steadily due to the Federal tax incentive and various state and local tax credits. Bioethanol production from lignocellulosic biomass is beginning to emerge due to recent advances in conversion technology. The same biotechnology revolution that is driving near-term commercialization will drive down the cost of bioethanol manufacture over the next 10 years. A point of cost competitiveness with the wholesale gasoline price of today will be reached based on the use of inexpensive residues [3].

POLICY DRIVERS TO INCREASE BIOENERGY AND BIOBASED PRODUCTS
The President issued Executive Order 13134 on August 12, 1999 to coordinate Federal efforts to accelerate the development of 21st century bio-based industries that use trees, crops, and agricultural and forestry wastes to make fuels, chemicals, and electricity. The

Order is titled "Developing and Promoting Biobased Products and Bioenergy". The Order and related Executive Memoranda [4] were based on extensive literature and findings [3, 5] from which the following can be concluded:

1. There is a sufficient supply of biomass materials to provide food, feed, fiber and some level of energy, fuels and materials. The precise level and impact of energy production varies but a tripling of biobased products and bioenergy by 2010 is a Presidential goal. By 2020, the goal is a tenfold increase.

2. Several drivers provide impetus to a bioenergy and biobased products effort. These include emerging market opportunities, increased rural development needs, reducing environmental impacts, increasing energy security and diversity, reduce fossil carbon emissions, and meeting the growing need for energy and materials with sustainable technologies.

3. Many companies developing bioenergy and biobased products are emerging and others are large and generally more mature (corn refining and pulp and paper). Because of the nascent nature of the "business" a large emphasis on research, development and deployment is needed.

4. There is no single agency, industry, or sector that can meet the challenges and needs to accomplish these aggressive goals on their own. All of these studies call for integrated efforts across federal agencies, current industrial sectors, academia, national laboratories, non-profit organizations, professional societies, public interest groups, etc.

Several Congressional bills have emerged with strong bipartisan support. These have aligned objectives with the Executive Order and Federal Agency actions. They are summarized below:

Bill	Date Introduced	Principal Sponsor	Summary	Status
S.935	4/30/99	Lugar (IN)	Would authorize $49 million a year for FY 2000-2005 for research into biobased products and chemicals.	Hearings held (Senate Agriculture, Nutrition and Forestry Committee)
H.R.2819	9/8/99	Udall (CO)	Biomass Research and Development Act of 1999. To create an initiative for research and development into the utilization of biomass for fuel and industrial products.	Referred to the Committee on Science, and to the Committee on Agriculture.
H.R.2827	9/9/99	Ewing (IL)	National Sustainable Fuels and Chemicals Act of 1999. Companion bill to Sen. Lugar's S.935.	Referred to the Committee on Agriculture, and to the Committee on Science.
S.1177	5/27/99	Harkin (IA)	Would amend the Food Security Act of 1985 to permit harvesting of crops on land subject to conservation reserve contracts for recovery of biomass used in energy production.	Referred to Senate Agriculture, Nutrition and Forestry Committee
S.882	4/27/99	Murkowski	Energy and Climate Policy Act of 1999. Strengthens provisions of the Energy Policy Act of 1992 and the Federal Nonnuclear Energy Research and Development Act of 1974 to promote voluntary efforts to reduce or avoid greenhouse gas emissions.	Referred to Committee on Energy and Natural Resources

NEAR-TERM INCREASED BIOMASS USE

Current industrial biomass use is primarily of residues of agriculture, forest products operations or urban and industrial residues. Additional crop residues could be collected for product or energy purposes. Additional increases in supply would have to come from

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crops specially planted for these purposes. Figure 3 shows an example of a supply curve considering the residues and at what point some dedicated feedstock supply is needed. Life cycle analysis of a dedicated poplar plantation and electricity production through an integrated gasification combined cycle shows that there are almost no net carbon emissions [6]. The current conventional energy values are also included.
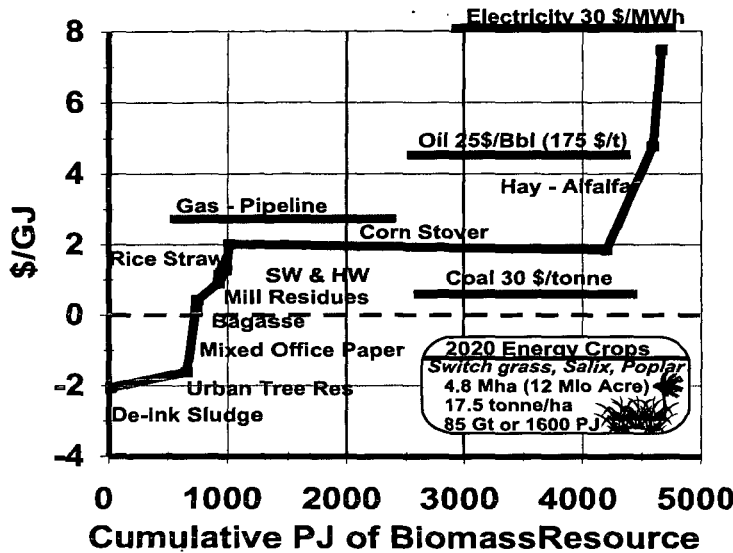

Figure 3. Supply curve of various biomass residues and dedicated feedstock plantations, for instance, of switchgrass, Salix, and poplars.

MULTIPLE ENERGY OPTIONS FROM BIOMASS

Biomass is a complex resource that can be processed in many ways leading to a variety of products. Biological routes can convert the carbohydrate portion of the lignocellulosic feedstock into ethanol, an oxygenate that can also be used as a fuel additive. The lignin component cannot be used this way and is combusted to generate heat and electricity. Gasification provides a way to generate syn-gas and from it the clean conventional fuels: Fischer Tropsch liquids, methanol, and others (see Figure 4).

Biomass Production ➡ **Biomass Processing** ➡ **Biomass Fuels** ➡ **Biomass Conversion**

Forestry
- thinning
- residues

Agriculture
- grain
- straws
- manures
- energy wood
- oil plants

Trade & Industry
- sawn industry residue
- wood industry residue
- used wood
- organic residue

Mechanical
- chipping
- cleaving
- pelleting
- briquetting
- pressing

Thermal and/or chemical
- drying
- gasification
- pyrolysis
- esterification

Biological
- alcohol fermentation
- methane fermentation

Solid Fuels
- pellets
- charcoal

Gaseous Fuels
- biogas
- wood gas
- hydrogen

Liquid Fuels
- ethanol
- methanol
- Fischer-Tropsch liquids
- oil from plants
- oil from pyrolysis
- esters

Heat
- single stove
- central heating
- heating plant

Electricity & Heat
- CHP plant with
  - steam turbine
  - gas turbine
  - steam & gas turbine
  - Stirling engine
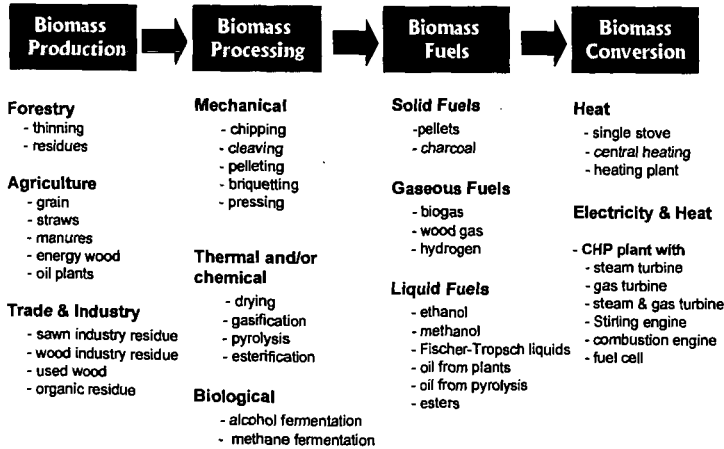 - combustion engine
  - fuel cell

Figure 4. From multiple biomass resources to a variety of fuels and energy products

A proxy for how well some of these various processes perform is the overall process efficiency starting with lignocellulosic biomass [7].

Fuels from Biomass	Efficiency (HHV)	Comment
Methanol	54	From gasification
Hydrogen	60	From gasification
Fischer-Tropsch liquids (FTL)	49	From gasification
FTL (single pass) + electricity	26.5 (FTL); 17.2 electricity	From gasification, lower capital costs
Ethanol	50% (1999); 63% (2015)	From hydrolysis and fermentation

LONG-TERM RENEWABLE HYDROGEN PRODUCTION TECHNOLOGIES

The use of solar energy to split water into oxygen and hydrogen is an attractive means to directly convert solar energy to chemical energy. Biological systems are reviewed below. There are also chemical and electrochemical systems that have long-term (>10 years), high-risk, high-payoff technologies for the sustainable production of hydrogen. These systems have been summarized by Padro [8]. The biological processes include:

1. Algal hydrogenases that evolve hydrogen at a rate that is 4 times that of the wild type, and are 3-4 times more oxygen tolerant [9].

2. Photosynthetic organisms with light harvesting, chlorophyll-protein complexes that effectively concentrate light and funnel energy for photosynthesis. These cells showed photosynthetic productivity (on a per chlorophyll basis) that was 6-7 times greater than the normally pigmented cells [10], a phenomenon that could lead to significant improvements in the efficiency of hydrogen production on a surface-area basis. Various reactor designs are under development for photobiological hydrogen production processes (single-stage vs two-stage, single organism vs dual organism) [11].

3. Systems to convert CO (found in synthesis gas) to hydrogen via the so-called water-gas shift reaction ($CO + H_2O = CO_2 + H_2$) at ambient temperatures. Microorganisms isolated from nature are used to reduce the level of CO to below detectable levels (0.1 ppm) at temperatures of around 25-50°C in a single reactor [12,13]. This process has significant potential to improve the economics of hydrogen production when combined with the thermal processing of biomass or other carbon-containing feeds.

THE ROLE OF RENEWABLE FUELS IN A CARBON-CONSTRAINED WORLD

Decarbonization of fossil fuels is a way to increase energy consumption without increasing carbon consumption in a carbon-constrained world. Removal of carbon from fossil fuels prior to use in energy production is likely to be far less costly than attempting to remove CO_2 from dispersed sources. If fossil fuels are converted to hydrogen in a central facility, the collection of CO_2 (or elemental carbon, depending on the process) is relatively simple compared to collecting CO_2 from every fossil-fuel-consuming vehicle on the road. Carbon neutral biomass-derived transportation fuels offer solutions to this.

CONCLUSIONS

For renewable processing of biomass or direct biological hydrogen production the cost of the technologies still needs to be decreased through research, development, demonstrations, and diffusion of commercialized new technologies. Valuing the environmental and social contributions that biomass inherently makes can also help increase its use. Broad societal consensus on land and water use issues is needed. Each route still requires significant integrated efforts across federal agencies, multiple industrial sectors, academia, national laboratories, non-profit organizations, professional societies, public interest groups, etc. The challenge to make renewable resources a major commercial reality is equated to putting the man in the moon. The versatility of biomass and conversion technologies makes it suitable to either adapt to today's fuel and vehicle

infrastructure or to be a part of a new infrastructure for hydrogen fuels and super efficient vehicles of the future.

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CATALYSIS AND OPPORTUNITIES FOR THE PRODUCTION OF H₂

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ABSTRACT

This presentation will describe the increasing importance of H₂ in our world. Since the bulk of the world's H₂ is produced by catalytic processes, often involving multiple types of catalysts, it is clear that catalysis plays a critical role in the production of H₂. The focus will be on the use of catalysis in the current and future production of H₂. Steam methane reforming will be a focal point of the discussion, and it is interesting to view the large number of catalysis steps that are used in this major technology. Some background will be provided to give a perspective of the dramatic change in the supply and demand for H₂ in the past decade, followed by a review of how it is produced commercially, with a view to how multiple types of catalysis contributes to the total process for H₂ production. Issues of carbon management and CO₂ emissions will also be discussed. In addition, some alternative catalytic approaches [fuel cells, photocatalysis, membrane reactors, etc] for H₂ production will be discussed and specific barriers to progress and opportunities for further research in this area.

INTRODUCTION

Hydrogen is forecast to become a major source of energy in the future. Prior to the early 1990s, H₂ was plentiful with refineries being major producers. Now that picture has changed due to environmental demands to reduce sulfur emissions and the production of less aromatics for gasoline; thus, refineries have had to build additional H₂ production units nearby [1]. H₂ offers the potential of a clean burning fuel if it is combined with only O₂ and would result in no extra CO₂ emissions, as long as H₂ were obtained from non-fossil fuels . With H₂ production being localized and without a large scale distribution system to move this hydrogen to more customers, H₂ is currently not a cheap fuel alternative; it simply has too much value as a chemical reductant. Limitations of space for this manuscript do not permit a complete discussion below of issues associated with the production of H₂; thus, the reader is encouraged to examine the references for greater detail.

Steam methane reforming, SMR, is the largest and generally the most economical means to produce H₂. SMR is not just one reaction, but a series of well balanced operations often including most of the following: desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and NOx removal. The key reaction is represented by equation 1. Several good reviews describe this and other commercial approaches to the

$$CH_4 + H_2O \rightarrow CO + 3 H_2 \qquad\qquad (1)$$

production of H₂ [2,3]. Since the desired product is H₂ and not CO, the CO is usually taken through the water gas shift reaction to produce more H₂ (equation 2). This produces CO₂; in

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad\qquad (2)$$

Table 1
Steps in SMR which employ catalysts [from reference 1]

Process operation	Temperature, °C
Sulfur conversion [HDS]	290-370
H₂S removal [ZnO]	340-390
Chloride removal [Al₂O₃]	25-400
Pre-reforming	300-525
Steam methane reforming	850
High temperature water gas shift	340-360
Low temperature water gas shift	200
Methanation	320
NOx removal [NH₃ SCR]	350

addition, one must consider that the heat derived to drive the very endothermic reaction'1, often comes from natural gas burners, which also produce more CO_2. There is an aggressive worldwide R&D effort to develop other cost effective and energy efficient means to produce H_2, especially for small volume use in remote areas of the world.

H_2 production is linked to CO_2 production when fossil fuels are reformed. In order to reduce CO_2 emissions, use of natural gas instead of coal [a higher C/H feedstock] is preferred if one must use a fossil fuel. Fuel cells as a source of power usually consume H_2. While fuel cells are widely promoted for their fuel efficiency, they must be assessed based upon the levels of CO_2 produced from the fuels used to power the fuel cell. In the near term, there is interest in using increased carbon sequestration to provide some intelligent carbon management approaches for fossil fuel routes to H_2. In the long term, we need to focus on the production of H_2 from non-fossil fuel sources or on truly renewable fuels.

There has been much excitement in the literature to use CO_2 as a feedstock to make chemicals. However, even if we had existing technology to covert CO_2 to more valued chemicals, the volume of chemicals would still be very small relative to the level of CO_2 emissions being discussed. Further, using H_2 on a massive scale to chemically reduce CO_2 to CO or CH_4 has questionable value because of the cost of the H_2. In addition, most of the world's H_2 is made from SMR which co-produces CO_2; thus it makes little sense to use SMR derived H_2 to reduce global CO_2 levels.

BARRIERS TO PROGRESS

In considering new approaches to H_2 production and/or SMR improvements, several technical barriers exist:

- Heat transfer seriously restricts operating temperatures
- More literature data needs to be gathered by studying reactions closer to the high pressure operations of existing processes and the demands for high pressure H_2
- Advances in reactor design are needed
- Overcoming limitations of material components with regard to metal dusting or high temperature seals
- Need for more ex-situ surface science techniques which allows one to characterize working catalysts under extreme temperatures [850°C] and pressures [400 psig]
- Developing process conditions which assure safe operation

OPPORTUNITIES FOR ADDITIONAL RESEARCH

Overcoming the barriers noted above will also open up new avenues for research, including:

- More laboratory units capable of studying SMR under actual process conditions
- Need for a simple, accelerated aging test to assess catalyst life
- More efficient ways to provide or utilize the energy needs for SMR
- Catalysts which minimize the formation of elemental carbon
- Non-fossil fuel sources for commercial H_2 production
- Use of CH_4 as a substitute for H_2 in the production of chemicals

ALTERNATIVE MEANS FOR PRODUCING H_2

Identifying the barriers, enables one to define new opportunities for research, not only for existing approaches but also for alternative means to produce H_2. While there is a need and demand for new routes to cost effective production of large volumes of high pressure H_2, there are niche opportunities where small volumes of low pressure, very pure H_2 are also attractive. Technologies which could address these needs [with some specific hurdles in brackets] include:

- methane decomposition [need to resolve how to handle and use all the huge amount of by-product carbon]
- use of membrane reactors [still limited by materials deficiencies, high temperature seals, and membrane configuration issues] [5]
- solar energy for electrolysis of water [must use visible light with high quantum yields]
- selective oxidation of methane [must provide convincing evidence for safe operation]
- oxidative dehydrogenation [issues of by-product coke formation which leads to fouling and an olefin co-product which must be in huge demand]

- biomass conversion [need pilot demonstration which addresses all the scale up, cost, and environmental issues]

SUMMARY

Steam methane reforming is the dominant technology for H_2 plants, and it comprises many different catalytic operations, including desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and deNOx. As long as natural gas and petroleum based hydrocarbons are still relatively low cost fuels, SMR will continue to be a cost effective approach for making H_2. Steam reforming is a mature technology, but there is fertile ground and room for technological improvement. Beyond 2010 future economic or environmental issues may eventually force adoption of substitute, alternative technologies since steam reforming is an energy intensive, endoergic process, CO_2 is a co-product, and H_2 purification is necessary. At the fundamental research level, there is a need for more catalyst studies at >20 atm where the chemistry is actually practiced and the bulk of customer demand exists. The life of the catalyst is an important criteria in benchmarking new catalysts versus commercial SMR catalysts and suitable accelerated aging tests need to be devised which provide meaningful assessments of alternative catalysts or technologies.

There are a number of emerging and attractive approaches to H_2 production, but the greatest opportunities in the future would seem to lie with non-fossil fuel based H_2 technologies, where major breakthroughs are needed. In considering new technologies for H_2 production, one has to consider the entire process. That is, one must have separation and purification steps, consider net energy demands and balance, the quality of the feed, etc. Ultimately, the route one chooses to produce H_2 will be a function of not only the technology advances, but also economics, the environment, specific customer needs, and market demands.

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Molecular and Molecular Assembling Approaches to Develop Efficient Catalytic Processes of Hydrocarbon Fuels

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Introduction

Hydrocarbon fuels are expected to play major roles to meet energy demands on the earth in the initial half of 21 century. Nevertheless, their efficient use and up-grading are strongly required to save the sources, and reduce environmental load. The up-graded products of the highest efficiency and least contaminants are designed through an adequate structural understanding of hydrocarbon fuels and their up-grading catalytic processes based on their structural information about the feeds, intermediates and products. Catalysts are the keys for up-grading processes. Designs of their adequate uses and materials for higher activity, selectivity and life are equally concerned.

Results and Discussion

Structural Understanding of Hydrocarbon Fuels and Molecular Understanding of Gasoline and Gas oils

Environmental regulation such S, N and aromatic contents as well as the combustion performance such as octane and cetane numbers require severer up-grading. The molecular basis reaction design which requires the reactivity of every constituents molecules is now studied by describing structure and contents of every molecules. GC-AED developed by Hewlett-Packard and Chevron is a powerful tool to analyze every molecules by classifying them according to their elemental composition detected by AED(atomic emission detector) after the separation by GC.

Figure 1 illustrates chromatograms of a gas oil by detecting C, S and N, respectively. Thus, the elemental composition of every species detected is obtained by this tool. By combining GC-MS to identify the molecular weight of the every peak, molecular composition of the peak is identified. There is, of course, limitation due to the chromatographic separation as shown in the N chromatogram where a broad hump is observed in a particular gas oil. The acid-extraction separates species in the hump from the other nitrogen species as basic nitrogen species, giving individual peaks to be identified as shown in Figure 2.

Figure 1. C, S and N chromatograms of MCO measured by GC-AED. C_n:normal paraffin with n number of C and C1~C4:1~4 substituted methyl groups.

Figure 2. Basic fraction of FSL extracted by sulfuric acid. Background was successfully removed and it was analyzed as quinoline and benzoquinoline derivatives using GC-MS.

Approaching to Molecular Understanding of Vacuum Gas Oil

Vacuum gas oil is an important feed stock to be further up-grading rather easily by catalytic cracking through hydrodesulfurization/hydrodenitrogenation and hydrocracking. Their molecular identification has not been achieved yet by GC-AED. However, narrow cut distillation and selective separation(nitrogen by acid extraction and sulfur by PdCl chromatogram) are expected to separate it suitable for GC-AED analyses.
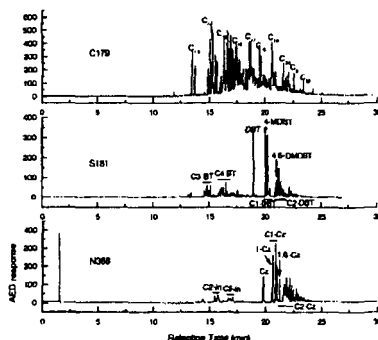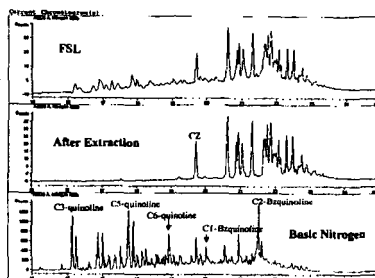
Molecular and Molecular Assembling Understanding of Resid and Coal

Resid and coal consist basically of polyaromatic-polynuclear macromolecules. The aromatic rings carry alkyl chains, being linked through methylene, aryl-aryl, ether, and thioether bonds. The aromatic ring carries also the heteroatoms within the ring. The sizes of molecules, aromatic ring and alkyl chains as well as the number of nuclei vary according to coals and crudes, although there are several trends which describe empirically such structural parameters.

Complex mixtures of molecular species in resid and coal carries parafins and naphthalenes of large molecular size. Such mixtures of macromolecules gather to form micelle or solid glass, through the intermolecular linkages. Hydrogen bonding, charge-transfer, alkyl entanglement and π-π ring stacking are proposed to exist. Figure 3 illustrates XRD profile of resid and coal. Definite diffractions are observed at around 20 and 26, which are ascribed to alkyl entanglement and π-π ring stacking.
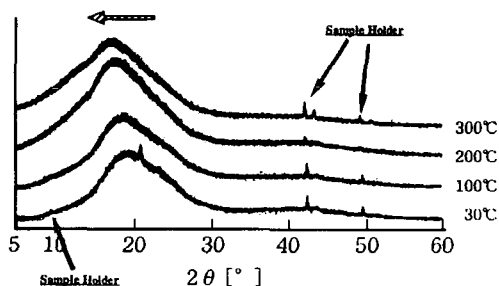

Figure 3. XRD of coal and resid (Measuring Temp. : 30~300°C, Step Scan : 4sec/0.01 °C, He atmosphere).

Resid and coal also carry same inorganic constituents. V=O and Ni porphyrins, minerals and ion-exchangeable cation are representative inorganic components in the former and latter fuels, respectively. Such inorganic constituents often provide bridges between macromolecules, or macromolecular chains.

Structure of Char
High molecular weight hydrocarbons tend to give char/coke when heated, liberating smaller molecules and cracked products. Such char/coke is a trouble maker as plugging and poisoning substances in the process, as well as combustible and gasifiable solid fuel. Their structure is also important to prevent their formation and to enhance the reactivity. Although the char/coke tends to carry some heteroatomic material when formed at lower temperature, it consists basically of hexagonal network. The size of hexagons and their stacking varied according to its experienced temperature, forming conditions and starting feed, approaching to the graphitic structure. Such microscopic stacking units gather to form micro domain, domain, and texture by orienting the microcrystallines and their assembles, respectively.

Recent development of high resolution SEM, TEM and STM/AFM in addition to XRD clarifies such micro, meso and macroscopic structure of char/coke. Figure 4 illustrates typical high resolution SEM, TEM and STM photographs of mesophase pitch based carbon fiber to show a series of structure.
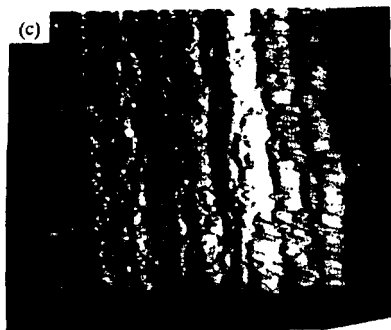
(c)
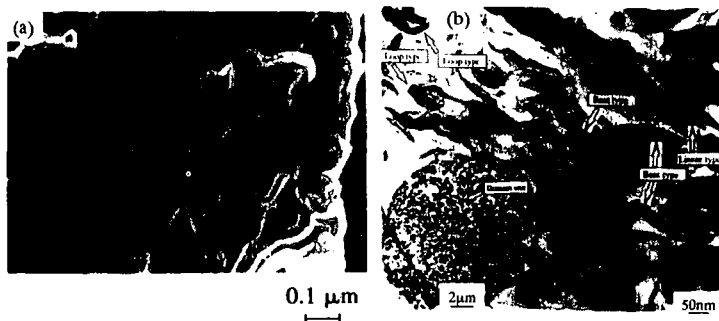
Figure 4. SEM, TEM and STM photographs of mesophase pitch based carbon fiber (a)HR-SEM photographs (outer section) (b)TEM BF images of the transverse section (total transverse image in the rectangular) (c)STM images of the longitudinal section.

Structural Understanding of Up-grading Schemes

Desulfurization and Denitrogenation of Gas Oil

The problem in the deep desulfurization of gas oil has been identified as the low reactivity of 4 and 6 alkyldibenzothiophenes. Their desulfurization has been proposed to proceed through hydrogenation of outer phenyl ring prior to the desulfurization at the relatively lower temperatures and direct desulfurization as another major desulfurization route at relatively higher temperatures.

GC-AED can follow the schemes of the substituents among other thousands of coexisting partners in the real feed which are strongly influenced by the coexisting partners as well as the catalyst performances. The former influences are defined as inhibitions which often restrict the deep desulfurization of the targeted level. Nitrogen and aromatic species, H_2S and NH_3 and their products are major inhibitors, their inhibiting factors being quantified to design the reactor, the process, and the catalyst. It is to be noted that the inhibitors are reactive to change their forms, strengthening or weakening the inhibition. GC-AED can also follow such change of structure and inhibitors at the same time.

Denitrogenation is also a target of refining. Reactivity, inhibition and susceptibility to inhibition of other nitrogen species are studied similarly. Figure 5 illustrates the reactivity of nitrogen species and the changes of their forms during the reaction, conforming the reaction scheme.
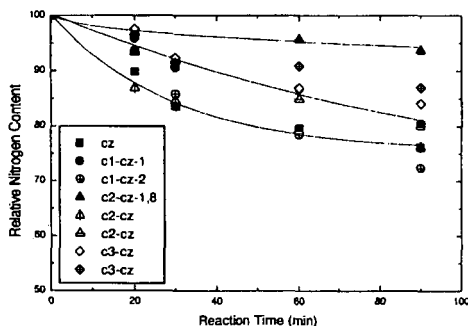

Figure 5. Reactivity of nitrogen species in FSL hydrotreated over $NiMo/Al_2O_3$ catalyst at 340 °C under 5Mpa of H_2. Background is removed in calculation. Number before and after symbol means number of methyl group and its location.

Desulfurization and Hydrocracking of Vacuum Residue and Coal Liquefaction

Longer term operation and higher middle distrate yield have been continually pursued in the desulfurization of vacuum residue. The reactivity of asphaltene for coking or strong adsorption as well as cracking, hydrogenation, desulfurization and removal of metals in asphaltene are major concerns. The higher conversion of asphaltene is a key to improve the efficiency in the coal liquefaction.

Changes of polymeric structure in the reaction suggest the route of distillate production. GC-AED is a powerful tool to identify the cracked products as the elemental parts of asphaltene.

Changes of asphatene tell us schemes for dry-sludge and coke/carbon formation. The authors are interested in clarifying by XRD the change in the entanglement and stretching of the asphaltene in the heated solvent through the hydrogenation, cracking, and dealkylation.

Reactivity of Char for Gasification

The reactivity of char, coke/coal or the graphite has been major research interest. However severer conditions in terms of temperature rather than the reaction, non-catalytic process and gasifying reagent appear to suggest that the reactivity is basically governed by rather physical fractors to influence the reactivity for gasifying conditions. The gasification of the next generation may revive the catalytic one under mild conditions to produce products of higher calorific value. The reactivity to achieve complete conversion of carbon may reflect the chemical structure of the hexagons and their assembles. The contact or holding and transfer of the catalyst are the other concerns.

Catalyst and Process Designs of Hydrocarbon Fuel Up-Grading

Deep desulfurization

Gasoline and diesel fuel have been regulated to carry S contents less than 30 and 50 ppm, respectively by the year around 2005. Desulfurization has been a major target of petroleum refinery, and further revolutional reduction of S is now within the scope.

Process and catalyst designs are equally pursued. According to the references, how to enhance the reactivity of refractory sulfur species and to reduce the inhibition are keys for the design.

Multi-stage processes have been proposed for this purpose. Reduction of product inhibition, in addition to selective activation of refractory sulfur species and suppression of partner's inhibition, is a key issue for the process. The author proposed a reactor of a novel concept as shown in Figure 6. There are problems to be solved in the catalyst form. Nevertheless, I believe it is possible and useful.

The removal of trace refractory species is another way to achieve deep desulfurization. The regeneration of remover and use of removed species are the tasks to be solved. Carbon with catalytic function can be a promising candidate for this purpose.

The catalyst for deep desulfurization has been continuously looked for. Higher activity of alumina supported sulfide has been achieved to satisfy the present regulation. Novel supports in addition to combinary sulfides can be targets to be studied. Acidity of the support is now concerned in the desulfurization in terms of hydrogenation, isomerization and resistivity against H_2S. Basic nitrogen species including NH_3 must be taken care of to reduce their inhibition and catalyst deactivation.
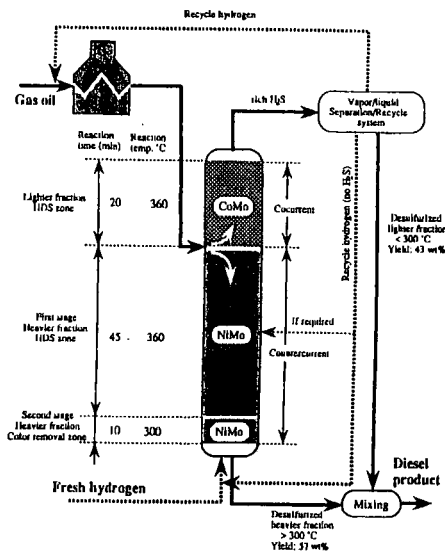

Figure 6. Deep HDS reactor design with cocurrent and countercurrent liquid-gas contact in separate catalyst beds.

Hydroprocessing of Vacuum Residues

Hydroprocessing of vacuum residue has been designed to consist of several steps, removal of solid contaminants such as NaCl and FeS, catalytic demetalation, catalytic modification of

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heavy asphaltene and catalytic desulfurization of whole VR including asphaltene. Removal of solid contaminants is very important for the life of the catalytic reaction, because they are triggers of coke plugging in the guard and catalyst bed front although the step is often ignored. Soluble precursors of the iron often pass through the filter to deposit on the guard where FeS accelerates physically and chemically the coke formation.

Deep demetalation and capacity of the demetalation agent are most wanted to prolong the continuous operation time. Better demetalation agents are strongly wanted. Chevron patented a moving bed demetalation, enlarging the capacity by continuous feed of the agent. Pore size is considered very important to accept heavy asphaltene which carries most of prophyrins. Large surface area to fix the metal sulfides is also important for large capacity. Hence pore size and surface area are compromised.

HDS of asphaltene requires also enough size of pores to asphaltene. Thus, the digestion of asphaltene is key factor of the hydroprocessing and hence liberation of micelle is particularly important. Otherwise only maltene and light asphalene are hydrotreated, leaving heavy asphaltene unreacted or thermally dealkylated, resulting in the formation of dry sludge.

The author has proposed prehydrogenation of asphaltene at lower temperatures to break mineral, reducing the coking to enhance the demetalation and HDS. Nano-particle carbon composite can be a candidate for these purposes. Such carbons carrying NiMoS have been proved an excellent catalyst for coal liquefaction. Low gravity allows the recovery from ash minerals after the liquefaction.

Catalytic Gasification

The author believes that the catalytic gasification of new generation is in time of development after the slugging and fluidized bed gasification. The catalytic activity of highly dispersed catalytic materials on the char surface has been reported remarkably high through the spillover mechanism. The difficulty of the catalytic gasification is how to keep the intimate contact between the catalyst molecules and chars both of which are usually solid of certain particle size. Fluidized bed of char in the catalyst bed materials may realize such a catalytic gasification. However the contact of the catalyst particle and the char is limited only at their outest surface, catalytic efficiency becoming so low. The formation of sulfate, chloride or even carbonate deactivates the catalyst. The present authors have proposed a catalytic missile of alkali metal which can go back and forth between char surface and support. Perovskite type oxide has been proved to play such a role of support. Another important feature is to activate the inactive form of the metal salts by virtue of catalytic reduction with char on the support surface. Such a reduction allows the repeated travel between the char and support. The demonstration by the moving bed is now under planning.

Conclusions

Fuel science in 21 century must emphasize three aspects.
1. Very basic understanding and problem shooting of on-going fuel processing technology
2. Support to the developing processes in terms of smooth operation with lower cost and better efficiency
3. New concepts for fuel processes of the next generation

Fuel science can help or create the novel processes and essential trouble shorts based on the better understanding of fuels and their natures at their fundamental levels.

Acknowledgement

Key words : hydrocarbon fuel, catalytic process, molecular approach.

SUPPRESSION OF NITROGEN OXIDES EMISSION BY CARBONACEOUS REDUCTANT

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Keywords: Coal Combustion, NO_x, Surface Complexes

Abstract
   For several decades many attempts have been made to suppress the NO_x emission from coal-fired power plant. In order to meet a more stringent environmental regulation in future, it is necessary to develop new technologies. In this paper, the effective measures achieved so far will be summarized and then the unsolved problems will be discussed. Among them, the understanding of the heterogeneous reactions, where char surface is involved, is not enough. Thus we have investigated the heterogeneous reactions of the NO_x formation and destruction over char surface. The formation of NO during coal char combustion was examined by paying attention to the role of surface nitrogen species on char. The reactions of model carbon with NO as well as N_2O were also examined both experimentally and theoretically.

The Present State of the Art
   In the 21st century, we may have to use more coal to meet the increasing energy demand, but unfortunately the use of coal results in many pollution problems. NO_x is the cause of acid rain, photochemical smog and greenhouse effect. N_2O is another important greenhouse gas and contributes to ozone depletion. The suppression of these gases is one of the most urgent subjects for us. Without any measures coal-fired power plant may emit NO_x of more than 700 ppm. Thanks to many efforts in the last 25 years, emission was reduced to a considerable extent. As primary measures, low NO_x burners, air staging (overfire air), fuel staging (reburning), flue gas recirculation and others were developed (Fig. 1), and selective catalytic reduction (SCR) or selective non-catalytic reduction are widely used as secondary measures [1]. Simply speaking, the purpose of these technologies is either to decrease NO_x formation by moderating combustion temperature or to enhance the reduction of NO_x once formed. Main reducing agents in furnace are hydrocarbon radicals and coal char, while NH_3 and urea are used to reduce NO_x in flue gas.
   The present state of the art can be summarized as follows. Primary measures achieve 30-70% reduction in NO_x when applied separately. Higher reductions, up to 90%, can be achieved with their combination. Therefore, the reduction to 150-200 ppm level is easily achieved in advanced coal-fired power stations without SCR unit. If these primary measures are combined with SCR, the emission level can be suppressed to as low as 50-70 ppm. The most recent study even claims the success of designing a burner to reduce the NO_x level below 100 ppm, by keeping the amount of unburnt carbon at 3 %. In Japan, legislation to limit NO_x emissions was enforced in 1970's, with more stringent standards in 1987. Occasionally even severer regulation is enforced by regional authority. Most frequently used primary measures are the combination of low NO_x burner and air staging. Sometimes flue gas recirculation or reburning is used in addition. SCR unit is also installed in many plants. The situations in other countries are quite different. For example, common power plants in the US use only low NO_x burners and the NO_x emission level is around 240 ppm.
   These technologies became possible only through a fundamental understanding of the formation and destruction mechanisms that affect the overall NO_x emission. It can be said that the principal mechanisms have been identified in most cases. The formation of thermal NO_x, Zeldovich NO_x, is initiated by the reaction between O radical with N_2 in air. Another source of thermal NO_x is known as prompt NO_x, where hydrocarbon radicals assist the decomposition of N_2 leading to the NO_x formation. The most important contribution to the overall NO_x emission in coal-fired plant comes from fuel nitrogen. About 75-90 % of NO_x is due to this source when low NO_x burner is used. The fate of fuel nitrogen is illustrated in Fig. 2. The volatile nitrogen and char nitrogen are oxidized to NO, and the NO is reduced by various reductants including char. The formation of NO_x from coal nitrogen is quite complex and not yet fully understood. The reduction of NO_x over char surface takes place to a significant extent. However, the contribution of this reaction on the overall NO_x reduction is not yet clear. The reaction mechanism, especially in high temperature zone, is also not well understood.
   Regulations for NO_x and N_2O will become more and more stringent in near future. Without knowing the detailed mechanism of the reactions occurring during coal combustion, it would be difficult to meet such regulations. The formation of NO_x from fuel nitrogen and the decomposition of NO_x over char surface should be elucidated. The N_2O formation and destruction mechanism is also important to find out the best way to reduce it. At present, there is no regulation on N_2O emission, but about 50 ppm of

N_2O is emitted from fluidized bed coal combustor.

The Scope of this Paper

Among all reactions occurring in coal-fired combustion system, the least clear parts are the char-related reactions. Formation of NO_x from char and the reduction of NO_x over char surface are understood only superficially. Therefore in order to get a clearer picture of these reactions, we have investigated the mechanism of C-NO_x reaction. For the purpose of simplification, we used PF char (phenol formaldehyde resin char) as a model of coal char. This does not have inherent nitrogen before the reaction. We have studied the reaction of PF char with NO, the reaction of PF char with N_2O, as well as the NO_x formation from coal char combustion. The computer simulation studies have also been carried out for these systems. In this presentation we would like to summarize our results and discuss the future direction related to this field.

The most unique feature of our study is that we have paid a special attention to the role of surface nitrogen species on char. Boldly speaking, combustion people are only interested in the formation of NO_x but not necessarily in the N_2 formation. This was deduced from the fact that many studies have used air as oxidizing gas. This is simply because air is used in practical combustion systems. Thus the formation of N_2 has been neglected and, as a result, the nitrogen mass balance has not been obtained. On the contrary, we are interested in the overall reaction pathways including the formation of N_2. Thus we used O_2-He mixture instead of O_2-N_2 mixture for the coal char combustion, and NO-He mixture for the study of C-NO reaction. Thus we could establish the accurate nitrogen mass balance. Through this attempt, the amount of nitrogen species on carbon surface during the reaction could be quantitatively determined. It is well known that such surface species play an important role in many carbon gasification reactions.

Reaction of PF Char with NO

We have studied the C-NO reaction from various aspects, and have made several new findings in these studies [2-5]. First, the accurate mass balance clearly showed the presence of nitrogen accumulated on carbon surface. Many studies had noticed the presence of such surface nitrogen species, but there had been neither direct evidence nor quantitative data. Not only from the mass balance, but also from the XPS analysis the presence of surface nitrogen species was confirmed very clearly. The reaction can be described as

$$C( ) + NO \quad \rightarrow \quad C(N) + C(O) \tag{1}$$

where C( ), C(N) and C(O) denote the surface free site, nitrogen and oxygen complexes, respectively. Then, the N_2 formation mechanism from C-NO reaction was identified in step response experiments using isotope gases. The reactant gas was switched from $^{14}N^{16}O$ to $^{15}N^{18}O$ during the reaction with PF char, and the product gases were analyzed (Fig. 3). The appearance of $^{14}N^{15}N$ immediately after the introduction of $^{15}N^{18}O$ strongly suggested that the main route for N_2 formation is as eq 2.

$$C(N) + NO \quad \rightarrow \quad N_2 + C(O) \tag{2}$$

This holds true in a wide range of temperature from 600 to 1000 °C. This study presented the elementary reaction step of N_2 formation for the first time. Before this study, it was thought rather ambiguously that N_2 is formed from two C(N) species.

Effect of O_2 on the Reaction of C-NO

In the coal combustion system, the NO reduction by char takes place more or less in the presence of O_2. The effect of O_2 on the C-NO reaction is very remarkable. For example, N_2 formation rate is significantly increased by the presence of O_2, and N_2O formation is greatly affected by O_2. Even though the reasons for these observations are not known, there has been almost no systematic study on the C-NO-O_2 system. We carried out step response experiments in the presence of O_2, and it was found that the main N_2 formation path is similar to eq 2 [6]. As for the N_2O formation during the C-NO reaction, many studies reported that there is no N_2O formation in the absence of O_2 [7]. On the contrary, we observed some N_2O formation in the absence of O_2. This finding is practically not so important, but from a fundamental point of view this is important for identifying the true reaction mechanism. We need to revise the former explanation for this reaction.

Simulation of C-NO Reaction by Molecular Orbital Theory

The chemisorption of NO molecule on carbon surface and the subsequent decomposition of the surface species were simulated by an *ab initio* molecular orbital theory (MO) [8]. For simplicity, single layer of polyaromatic compounds was employed as a model for carbon. The MO calculation of the system including both the model carbon and NO molecule was made, and its geometrical parameters were optimized. The adsorption of NO on carbon edge sites resulted in the formation of several types of stable NO containing complexes, C(NO). To elucidate the N_2 formation route from the

surface nitrogen complexes, one more molecule of NO was put on the N atom of the C(NO) species. The MO calculation predicted the formation of six-member ring complex including NNO bonding. The bond population analysis predicted that N_2 desorption from such complex is very probable. The N-O bond is so weak as seen in Fig. 4 that C(NN) complex will be formed. The C-N bond in the resultant species is much weaker than N-N bond, and it can be easily dissociated to release N_2 molecule. This reaction scheme is exactly the same as eq 2, which was experimentally implied.

Reaction of PF Char with N_2O

Compared with the reaction with NO, the reduction of N_2O by carbon and the formation of N_2O from coal char are investigated to lesser extent. These reactions are not important at high temperature combustion, but very important for low temperature process like fluidized bed combustion.

In the case of the reduction of N_2O by carbon, it has been assumed that N_2 is produced from N_2O without any bond breaking between two nitrogen atoms, although there was no direct evidence. We have carried out a step response experiment, and found the reaction mechanism being eq 3 as was expected. There is little N≡N splitting during $C-N_2O$ reaction [9].

$$C(\ ) + N_2O \quad \rightarrow \quad C(O) + N_2 \tag{3}$$

In MO simulation study, the calculation predicted the release of N_2 and the formation of C(O) when N_2O was put on the carbon edge [8]. This is again in agreement with the experimental observation.

NO_x Formation from Coal Char Combustion

As a result of recent development in low NO_x burner, the contribution of coal nitrogen to NO emission is of significant importance. In particular, the char nitrogen is the major contributor to the overall NO emissions. Therefore many studies have been carried out in relation to this reaction, and the importance of secondary reactions is suggested [10]. However, few researchers have shown an interest in the quantitative analysis of secondary reactions. We have carried out the reaction of coal char with O_2 in a fixed-bed reactor until the complete conversion of char, and established the mass balance. Fig. 5 shows the result of isothermal reaction at 850 °C with different bed heights. Several common features are noteworthy; (1) as a total, the major product was N_2, followed by NO, with a very small amount of N_2O, (2) the ratio of NO/N_2 was very small at the beginning but became almost unity at the final stage of reaction, and (3) the ratio decreased with increasing bed height. All of these observations can be explained if the occurrence of secondary reaction on char surface is assumed. We would like to emphasize again the important role of surface nitrogen species in this reaction. NO is expected to be the primary nitrogen-containing product from char combustion. NO thus produced would react with the char in the downstream to produce C(N), which then react with another NO to produce N_2 as in eq 2. If the remaining char became less and less, NO would escape from the bed without being converted to N_2. Thus the fractional conversion of char nitrogen to NO increased with char burn-off. This is in contrast with the observation by De Soete who reported that the fractional conversion of char nitrogen to NO was approximately proportional to the carbon burn-off [11]. This is probably due to the difference in reactor type, but further work is required.

Future Subjects

We now realize that we do not know much about the char-related NO_x reactions. We have to further investigate what actually happens in combustor. Especially the reaction behavior of char rapidly heated to high temperature should be explored. Through these studies, we may be able to design a better combustor with a lower NO_x emission.

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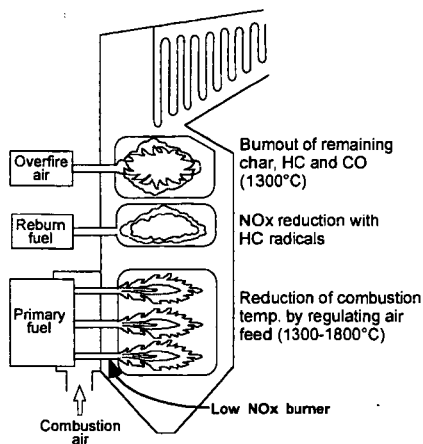
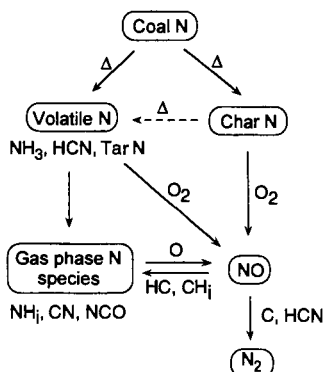Figure 1. Advanced utility boiler with various measures for NO_x reduction.

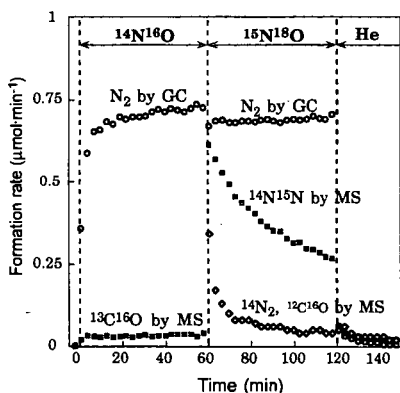Figure 2. Reaction pathways to the formation of NO and N_2 from coal nitrogen.

Figure 3. N_2 evolution profile during a step response experiment for C-NO reaction at 850 °C.
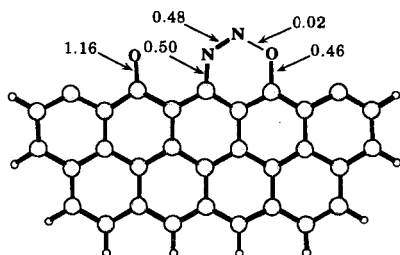

Figure 4. Stable structure of carbon with two NO molecules, suggested by MO simulation. Numbers indicate parameter of bond strength.
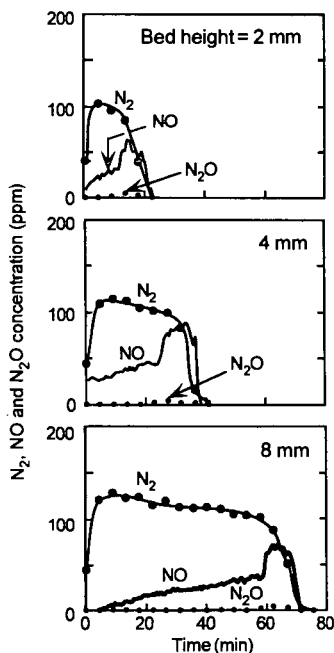

Figure 5. Effect of bed height on the gas evolution during O_2 gasification of coal char at 850 °C.

CHARACTERIZATION AND REACTIVITY OF ORGANICALLY BOUND SULFUR AND NITROGEN IN FOSSIL FUELS

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Introduction

The chemistries of organically bound sulfur and nitrogen forms impact significantly on the reactivity of and utilization strategy for fossil fuels. Previous inability to speciate and quantify the chemical forms of these heteroatoms coupled with the lack of a suite of standardized, well preserved, well characterized coals of varying rank limited the gaining of understanding of important fundamental chemical mechanisms. Advances in X-ray instrumentation over the last decade, along with the establishment of the Argonne Premium Coal Sample Program have allowed the determination and quantification of organically bound sulfur and nitrogen forms in fossil fuels and has led to deeper understanding of their reactivities. This paper reviews recent technical advances in this area and highlights several areas were significant progress in chemical understanding has been achieved and speculates about future trends.

Organically Bound Sulfur Characterization

In the last decade, major advances have been made in speciating and quantifying forms of organically bound sulfur in fossil fuels, involving both reactive and direct measurements. One reactive method uses flash pyrolysis[1], while the direct measurements involve XPS[2], K-Edge X-ray Absorption Near Edge Structure Spectroscopy (XANES)[3, 4] and L-Edge XANES[5]. The XPS and sulfur K-edge XANES methods were used to determine the forms of sulfur in the suite of Argonne Premium coals[6], and the results from XPS and two different K-edge XANES methods are plotted together in Figure 1. The accuracy of the latter methods is reported to be ±10 mole%. It was concluded that in low rank coals there are significant amounts of aliphatic sulfur (i.e., dialkylsulfides), and that levels of aromatic sulfur (i.e., thiophenes and diarylsulfides) increase directly as a function of increasing rank [3, 4]. The X-ray methods have been used to follow the chemistry of organically bound sulfur under mild oxidation in air[7], where it was shown that the aliphatic sulfur oxidizes in air much more rapidly than the aromatic sulfur, pyrolysis [8, 9], single electron transfer and strong base[10] conditions. Recently, results from the XPS and K-edge XANES methods have been shown to compare favorably with those from flash pyrolysis[11], mass spectrometry[12], and temperature programmed reduction (TPR)[13, 14]. This is a particularly important development since an approach to sulfur speciation using these techniques may be much more readily available than X-ray methods. In the future, speciation and quantification of organically bound sulfur by a pyrolysis GC/MS analysis or TPR approach may develop into a standard laboratory method.

Organically Bound Nitrogen Characterization

It is necessary to know how nitrogen is incorporated in the organic matrix, since it has been apparent for some time that nitrogen species play a role in coal asphaltene behavior[15] and in coal conversion chemistry[16]. X-Ray Photoelectron Spectroscopy (XPS) was used to speciate and quantify accurately the forms of organically bound nitrogen[17, 18], including the basic pyridines and quinolines and the weakly acidic or neutral indoles and carbazoles. These measurements, done on a suite of UK coals containing 80wt% or more carbon, indicate that basic nitrogen increases as pyrrolic nitrogen decreases as a function of carbon content. The organically bound nitrogen forms in the Argonne Premium coal samples[6] were determined by XPS[19]. The quantitative distributions of nitrogen types in Argonne Premium coals from XPS analyses are plotted in Figure 2 as a function of wt% Carbon. For fresh Argonne Premium coals, pyrrolic nitrogen was found to be the most abundant form of organically bound nitrogen, followed by pyridinic, and quaternary types. It is clear from Figure 2 that the distributions are rank-dependent, with the highest abundance of quaternary nitrogen in the lowest rank coals. The concentrations of this form decrease while pyridinic, or basic nitrogen forms appear to increase correspondingly as a function of increasing rank. The quaternary species were attributed to protonated pyridinic or basic nitrogen species associated with hydroxyl groups from carboxylic acids or phenols[19]. Similar distributions from XPS analysis of coal as a function of rank were independently confirmed [32]. The predominance of pyrrolic and pyridinic nitrogen forms in Argonne

Premium coal was verified by recent desorption high-resolution mass spectrometry both with whole coals and their pyridine extracts [33]. The sensitivity of the XPS approach for amino nitrogen species in fossil material has been established [28, 29]. Samples of recent sediments with up to 45% amino nitrogen [29] and pyrolysis tars of kerogen with up to 33% amino nitrogen [28] have been reported.

X-ray Absorption Near Edge Structure spectroscopy (XANES) has also been used for characterization of nitrogen forms in petroleum asphaltenes[20a] and Argonne Premium coals[20b]. These early nitrogen XANES results are not in total accord with those from XPS. Pyrrolic nitrogen appears to be the major form of organically bound nitrogen measured by both techniques. However, the XANES results report, in addition to pyrrolic and pyridinic nitrogen, the presence of aromatic amines and also pyridone forms, the latter in amounts similar to pyridinic nitrogen. In addition, the XANES results do not report the presence of quaternary nitrogen. While the XPS results were largely confirmed by high resolution mass spectrometry[33], opportunities remain for further development of an XANES approach for nitrogen speciation.

Solid state ^{15}N nmr offers much promise for characterizing nitrogen forms. The difficulties in developing a solid state ^{15}N nmr technique for the characterization of nitrogen forms in coals have been discussed, and progress is being made[21]. An earlier attempt to characterize the nitrogen forms in three Penn State coal bank coals by solid state ^{15}N nmr reported the observation of pyrrolic but not pyridinic nitrogen forms[22]. This appeared to be in contradiction with XPS and XANES data, however more careful work on Argonne Premium coals and their acidified derivatives showed the presence of pyridinic nitrogens. In the future, it is expected that the current hurdles will be overcome and that the technique will be used almost routinely for characterizing organically bound nitrogen forms.

X-ray Photoelectron Spectroscopy (XPS) was used to help define the possible correlation between the functional forms of nitrogen in coals and the formation of NO_x precursors during combustion processes [23, 30, 31]. These studies showed that the impact of structural variation in nitrogen forms initially present in coal was secondary to the effect of other coal combustion factors [30, 31]. XPS has also been used to characterize the forms of nitrogen found on carbon surfaces after treatment with NO_x [24]. XPS was used to identify and quantify the changes in organically bound nitrogen forms initially present in the Argonne coals in their tars and chars after pyrolysis[25]. In that study, coals were pyrolyzed in a temperature programmed decomposition (TPD) apparatus[26] at 0.23°C per second up to a specified temperature then cooled. Several temperatures from 400-810°C were chosen. Tars and chars from each pyrolysis temperature were collected and analyzed for nitrogen forms distribution by XPS. The reproducibility and repeatability of the nitrogen curve resolution results (± 3 mole %) is the same as in a previous investigation of fresh Argonne premium coal samples[19]. Representative changes in the nitrogen forms in two Argonne coal chars as a function of temperature are shown in Figure 3. Some of the quaternary nitrogen species are lost at the very earliest stage of pyrolysis, however, the major changes occur over a relatively narrow temperature range (600-700°C). Above 600°C the loss of pyrrolic forms is accompanied by a rise in the relative number of quaternary nitrogen forms in the chars, as noted by Pels, *et al.*[27] and Kambara, *et al.*,[23], and the quaternary and pyridinic nitrogen forms become the dominant forms in severely pyrolyzed chars. The significant disappearance of pyrrolic nitrogen in these high temperature chars confirms the suggestion of Pels, *et al.*[27], that pyrrolic nitrogen is partly converted into pyridinic nitrogen. Quaternary forms are proposed to arise from incorporation of pyridinic nitrogen into the growing polynuclear aromatic structures.

Future Outlook
In summary, methods are available today to get the kind of detailed information on important coal structural features that was not available just a few years ago. They are been applied to a standard suite of coals, and this represents an important advance in order to define the parametric variations as a function of coal rank. Exciting new opportunities now exist for elucidating and understanding the detailed chemistry taking place during conversion procedures by using these methods to characterize the reaction products as well as the starting coals. Mechanistic inferences and structure-reactivity relationships can be built based on this information.

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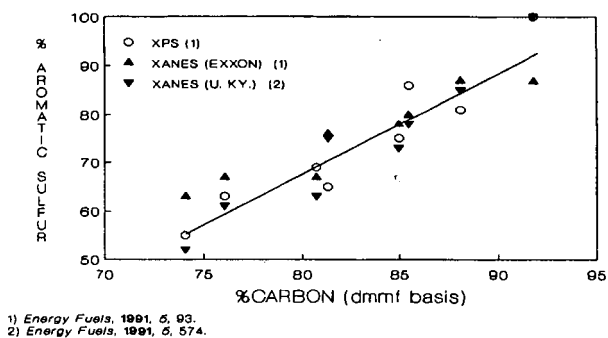1) *Energy Fuels*, 1991, *5*, 93.
2) *Energy Fuels*, 1991, *5*, 574.

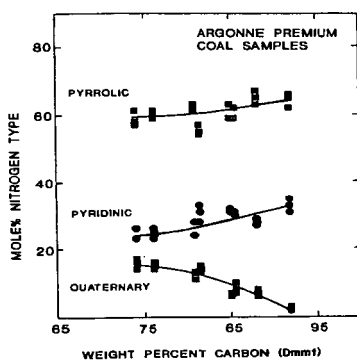Figure 1. Organic Sulfur Speciation and Quantification by S-XANES (refs. 3, 4)

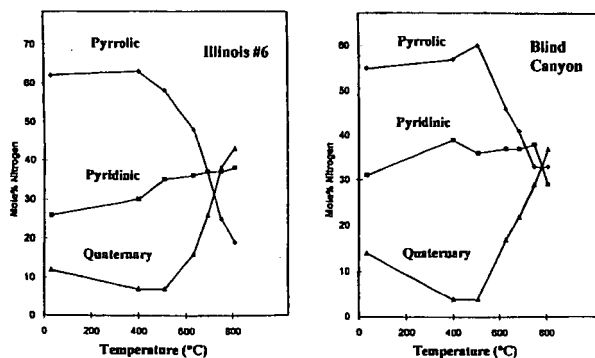Figure 2. Organic Nitrogen Speciation and Quantification by XPS. (ref. 19)

Figure 3. Tracking the Reactivity of Organically Bound Nitrogen Species (ref. 25)

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